BENZIDINE HYDROCHLORIDE METHOD FOR SULPHATES AS APPLIED TO WATER ANALYSIS

BY

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In ordinary routine boiler water analysis it is necessary to know the sulphate content of the water. The methods now in common use require considerable time and, therefore, do not meet the needs when the time for an analysis is short. With the idea in mind, therefore, of reducing the time of a sulphate analysis where conditions demand it, the use of benzidine hydrochloride as a precipitating agent was investigated.

The benzidine hydrochloride method for the determination of sulphates depends upon the fact that benzidine in the presence of sulphates forms a silky crystalline precipitate of benzidine sulphate, which being insoluble in water, can be filtered off, suspended in water and titrated in the hot with standard alkali, using phenolphthalein as an indicator. This titration is made possible by the very weak basic properties of benzidine. The operation can be completed in 30 minutes.

Benzidine is diamido-diphenyl: $C_{12}H_8(NH_2)_2$. It is a white crystalline salt, slightly soluble in water

but readily in hydrochloric acid, because of the formation of an addition product:- thus $C_{12}H_8(NH_2)_2$.HCl. In the presence of sulphuric acid, the hydrochloric acid is easily replaced, and we get the insoluble addition product with the sulphate. This sulphate is insoluble in the presence of an excess of benzidine hydrochloride, but readily soluble in hot water. By using phenolphthalein, and a standard alkali, the sulphuric acid can readily be titrated.

--HISTORICAL--

Vaubel[1] noticed that benzidine gave a precipitate of benzidine sulphate with soluble sulphate, but concluded that the solubility of the sulphate was too great to make use of the fact in practical work. Couturier[2] used benzidine in the estimation of sulphate by measuring the nitrogen gas given off by diazotizing the filtrate. The method, however, was too cumbersome for practical work. Müller[3], following up Vaubel's work, noticed that benzidine sulphate was insoluble in the presence of an excess of benzidine, and that a quantitative splitting off of the SO_4 radicle occurred in the presence of HCl. By working in neutral solutions and using known amounts of the benzidine hydrochloride

(whose exact titer was known) he titrated the excess of the benzidine hydrochloride in the filtrate with a standard alkali. Knowing the amount of precipitant started with, and the amount in the filtrate, the amount reacting with the SO_4, and consequently the amount of SO_4 was readily calculated. This method was not applicable in the presence of Aluminum, Iron, and Zinc, because solutions of the salts of these metals are acid. Furthermore, the adsorption of the benzidine hydrochloride in the cold is considerable. In order to avoid this, precipitation was done in the hot and the solution filtered in the cold.

Raschig[4] modified Müller's method in several respects. Instead of titrating the excess of benzidine hydrochloride in the filtrate, he filtered by means of a suction and titrated the precipitate in the hot with a standard alkali. This procedure eliminated working in neutral solutions. By using a weaker solution of benzidine hydrochloride and a larger reaction volume, the adsorption error was eliminated. An excess of benzidine hydrochloride reduced the solubility of benzidine sulphate to a minimum. Furthermore, this method is applicable in the presence of all metals except Ferric Iron, which seems to have some deleterious

effect upon the precipitate.

Raschig's procedure was as follows:-

> Benzidine solution is made up by triturating 40 gms. of the base in 40 cc. of water. Pour into liter flask; add 50 cc. HCl (1.19); make up to mark; dilute 20 times. 150 cc. = .1 g. H_2SO_4.
>
> Add the neutral or acid solution to the 150 cc. of benzidine. Stir. Allow to stand 15 min. Filter with suction. Rinse 2 times with small amount of water. Return ppt. to Erlenmeyer flask. Shake to remove from filter. Heat to boiling and titrate with N/20 HCl using phenolphthalein.

Müller[5] opposed Raschig's method on the basis that Benzidine sulphate is soluble in cold water and that washing the precipitate introduced too large an error. Raschig[6] points out that this error can be eliminated by using good suction in order to remove completely the mother liquid in which case only the smallest amount of wash water is required. In fact he points out that results showing an error of only .5% can be obtained by using no wash water at all. Suction, therefore, plays an important role in the process, removing the excess benzidine which would otherwise react with the added NaOH. Raschig further pointed out that it is better to work in neutral solutions, and in a volume of 400 cc. with an excess of benzidine hydrochloride. Ferric

iron causes low results; by reduction to ferrous iron, the disturbing influence is removed.

Friedham and Nydegger[7] studied Raschig's method carefully and came to the conclusion that it was applicable under all ordinary conditions. Errors occurred in the method but under suitable conditions they compensated each other. The principal errors are:-

1. Solubility of benzidine sulphate in water.
2. Adsorption of benzidine hydrochloride by the benzidine sulphate.

By using a constant reaction volume and employing a definate excess of the reagent, the error resulting from these two sources can be reduced to a minimum. Regarding iron, these authors believe that the iron reacts with the benzidine but if an excess over and above that required for the iron is added good results are obtainable. The concentration of the iron should not exceed 1 to 2 moles for 1 mole of sulphuric acid present.

The benzidine solution employed by these authors was made from the hydrochloride. 8.89 gms. of the chloride (equiv. to 6.7 gms. of the base) was dissolved in 20 cc. HCl (1.12) and diluted to 1 liter (1cc. = .00338 gms. H_2SO_4.) The solution in which the sulphate was to be determined was diluted to contain .1% H_2SO_4, and a 50% excess of benzidine solution added.

The whole was allowed to stand 15 minutes and the procedure carried out as stated above in the Raschig method.

--EXPERIMENTAL--

Before trying the method on waters some of the work of Friedham and Nydegger was repeated in order to become familiar with the technic. (a) Weaker solutions of sodium sulphate, however, were used than the above mentioned authors employed. The limits taken were those amounts of sulphate likely to be weighed in an ordinary water analysis:-namely, up to 500 parts per million of SO_4. Freidham and Nydegger worked with solutions containing 1000 parts per million of SO_4. (b) The use of weak and concentrated solutions of benzidine, and the effect of the volume of the liquid in which precipitation took place, was studied with the idea of reducing the volume to be filtered to a minimum. All the above mentioned workers used volumes varying from 400 to 750 cc., and solutions of benzidine hydrochloride containing 2 grams per liter. (c) With these points determined a revised method was formulated and applied to waters whose chemical composition was known, the results obtained being checked with the barium chloride method. From these experiments, information regarding the effect of iron and bicarbonate alkalinity on the re-

sults, was obtained.

The method at first used was as follows:-To 250 cc. of the water to be tested, 150 cc. of the benzidine hydrochloride solution (2 grams per liter) was added. The solution was stirred; allowed to settle; filtered rapidly by means of suction; and washed with about 25 cc. of water. The precipitate was returned to the beaker; water added and the mixture heated to boiling and titrated with N/20 NaOH using phenolphthalein as the indicator. Rapid filtration was best accomplished by filtering on a disc of filter paper (preferably Schleicher-Schüll No.589) placed in a Gooch crucible and protected by a Witt plate.

The influence of concentration of benzidine hydrochloride was first determined. For this work a N/10 solution of sodium sulphate was used, being prepared by exactly neutralizing a given quantity of N/10 sulphuric acid with N/10 sodium hydroxide. Suitable portions of this solution were diluted with distilled water to give four solutions containing the following amounts of SO_4 in parts per million: 48, 96, 192, and 480. Using an excess of 10, 15, 25, 35, 45, and 60% of benzidine hydrochloride, a series of sulphate determinations were made on each of the four solutions, 250 cc. being taken for each determination.

Table No. 1 contains the average of three determinations in each series. Judging from these results, an excess of not less than 25% of benzidine hydrochloride appears satisfactory in obtaining a complete precipitation.

Table No. 1.

Sulphate in Sodium Sulphate by means of Benzidine hydrochloride.

Volumes of solution taken 250 cc.
Total volume 500 cc.
Benzidine hydrochloride 2 gm.per liter.

Excess benzidine hydrochloride	Parts per Million SO_4			
	48	96	192	480
10%	26	80	180	400
15%	38	88	186	460
25%	48	96	192	480
35%	48	96	192	480
45%	48	96	192	480
60%	48	96	192	480

With the idea of reducing the volume of liquid to be filtered, a stronger solution of benzidine hydrochloride (8 grams benzidine per liter) was tried with the results as shown in Table 2.

Table 2.

Sulphate in Sodium Sulphate by means of Benzidine Hydrochloride.

Benzidine hydrochloride, 8 gms. per 1.
30% excess used in each determination.
Total volume, 300 cc.

Parts per million of SO_4	Excess Benzidine hydrochloride	SO_4 found	Error
10	30%	10.1	+0.80
24	"	23.6	+0.30
48	"	49.6	1.20
96	"	97.6	1.60
120	"	121.6	1.30
240	"	244.8	2.00
360	"	366.0	1.10
480	"	488.0	1.70

The results seem to be quite as accurate as those obtained with the weaker solution, so that in all of the subsequent work the stronger solution of benzidine hydrochloride was used.

For the purpose of investigating the adaptability and accuracy of the method in determining sulphates in natural waters, the method was used in parallel with the quick precipitation of sulphates by barium chloride on about 100 waters of varying composition.

The procedure with benzidine hydrochloride was the same as previously outlined with the exception that the strong benzidine hydrochloride solution (8 grams benzidine per liter) was used, and that 10 cc. of a 1% hydroxylamine hydrochloride solution was added in those waters that contained ferric iron. The ferric iron, as

pointed out by Raschig[6] reacts with the benzidine hydrochloride in such a manner as to give rise to low results. Ferrous iron, however, does not have this disturbing influence. By using hydroxylamine hydrochloride the ferric iron present can be readily reduced to the ferrous condition. The hydroxylamine will not react with the benzidine hydrochloride[6].

Using barium chloride, the procedure was as follows: 250 cc. of the water to be tested was evaporated to dryness in a casserole. The residue was moistened with 5 cc. of concentrated HCl, diluted with hot water and filtered. The filtrate was made up to 200 cc., and after heating to boiling, 10 cc. of barium chloride solution (52 grams per liter) was added at once with vigorous stirring. After allowing the precipitate to settle over night, the $BaSO_4$ was filtered off on to a Gooch crucible; dried at 180° C; ignited 5 minutes on a Meeker burner; and weighed.

Table No. 3 contains a few typical results. The results obtained by both methods agree close enough for all practical purposes. The benzidine hydrochloride method, however, has the advantage, since with it results can be had in 30 minutes, while with the barium chloride method 6 hours, and more generally 12, are required.

Table 4 contains a complete analysis of the waters used in Table 3, and will give some idea of the character of the waters on which the method was used. The methods used for this work were those outlined in the Standard Methods of Water Analysis published by the American Public Health Association.

Table 3.

Comparison of Results obtained with Barium Chloride and Benzidine.

Results expressed in parts per million

Lab. No.	SO_4 by $BaCl_2$	SO_4 by Benzidine	Difference
6678	80.6	84.5	+3.9
6682	76.5	80.6	+4.1
6723	254.2	257.3	+3.1
6729	87.6	96.0	+8.4
6742	68.7	76.8	+8.1
6804	45.4	40.3	-5.1
6887	584.7	583.7	-1.0
6942	62.2	63.4	+1.2
7081	29.6	32.6	+3.0
7082	173.2	180.5	+7.3
7084	343.9	341.5	-2.4
7087	101.2	107.5	+6.3
7114	51.0	46.0	-5.0
7128	19.8	15.4	-4.4
7139	38.8	38.4	-0.4
7142	24.7	19.2	-5.5
7144	48.0	46.0	-2.0
7148	16.2	21.0	+4.8
7155	26.3	25.0	-1.3
7156	51.8	63.4	+1.6

Table 4.

Composition of Water Analyzed.
Results expressed in parts per million.

Lab. No.	City	Total Solids	Fe	Ca	Mg	Na	Cl	HCO_3	SO_4	NO_3
6678	Atchison	342	4.0	47.6	19.8	---	10.	119.5	80.6	.5
6682	Arkansas City	800	0.3	116.9	20.3	207	240.	268.0	76.5	2.0
6723	Waldo	873	---	---	--	---	4.4	307.8	254.2	1.5
6729	Pittsburg	329	5.0	66.5	2.0	141	88.	330.0	87.6	---
2742	Hutchinson	915	9.5	107.0	31.7	243	406.	264.0	68.7	.5
6804	Osborne	464	2.5	109.0	14.4	31	19.	393.0	45.4	4.0
6887	Washington	1297	15.2	154.7	22.7		44.	266.0	584.7	1.0
6942	St. Marys	582	0.5	58.5	26.8	71	46.	376.0	62.2	6.0
7081	St. Francis	268	1.4	56.7	9.1	28	30.	224.5	29.5	1.2
7084	Cimarron	844	---	---	--	---	52.	244.0	343.9	0.0
7114	Winfield	241	8.4	55.0	10.8	---	20.	176.0	51.0	.5
7087	Mineral	1005	1.0	61.3	32.2	273	344.	391.0	101.2	---
7128	Kanopolis	301	1.0				10.	187.8	19.8	10.0
7139	Junction City	332	1.2	52.0	19.8	55	34.	295.5	39.8	.5
7142	Ellis	373	1.2	78.0	14.6	33	12.	312.5	24.7	1.0
7144	Turon	803	1.0				320.	246.5	46.0	1.0
7148	Neodesha	184.	1.2	59.0	13.0		20.	214.7	21.0	.7
7155	Abilene	215	1.2	40.5	9.8	11	14.	156.0	25.0	1.0
7156	Blue Rapids	394	1.2	37.0	23.0	72	18.	330.0	63.4	.7

Two things should be noted in Table 4. Ferric iron was present in all the waters, varying from 1.2 p.p.m. up to 15 p.p.m. Its presence, however, seems to have had no effect upon the precipitation of the sulphates as can be seen by examining Table 3. The bicarbonate alkalinity, too, varied from 119 p.p.m. up to 391 p.p.m. but the SO_4 results with the water containing the largest amounts are just as accurate as those containing smaller quantities. From this we can conclude that the HCO_3 has no effect upon the determination of SO_4 by benzidine hydrochloride. Furthermore, the final volume of a determination need not exceed 300 cc. as the results in Table 4 indicate.

Several precautions are necessary in order to obviate difficulty in carrying out the method. The precipitate should not be allowed to stand too long, for the silky precipitate turns to flakes on standing, which only dissolve after considerable boiling. The suction should be strong enough to remove the last traces of the mother liquid before any wash water is added. If it is not too high results will be obtained.

After transfering the precipitate, the water should be heated preferably until all the ppt. is dissolved. Altho this is not always necessary it is sometimes a safe procedure to insure easier splitting off of the HCl groups.

For ordinary routine water analysis the following procedure is recommended: To 250 cc. of the water (less if the SO_4 content is greater than 500 parts per million) add 10 cc. of a 1% solution of hydroxylamine hydrochloride (more if the iron content of the water is very high) and 20 cc. of benzidine hydrochloride. Stir vigorously and allow the silky white precipitate to settle. Filter on a disc of Black Ribbon Filter Paper in a Gooch crucible with suction. Wash with cold distilled water twice, (about 25 cc), and drain precipitate thoroly. Transfer the precipitate to the original beaker, add water and heat to boiling. Titrate with N/20 NaOH using phenolphthalein as the indicator. Parts per million SO_4 = 9.6 x cc. N/20 NaOH.

The benzidine hydrochloride solution is made up as follows: Place 8 grams of benzidine in an agate mortar, and add enough water to make a paste. Wash the paste into a one liter flask, add 10 cc. concentrated HCl, and make up to the mark. Filter if necessary. 1 cc. = .0026 grams SO_4.

--CONCLUSIONS--

1. The benzidine hydrochloride method is applicable for the determination of sulphates in water.

2. The results with the use of benzidine hydrochloride compare favorably with those obtained with the use of barium chloride.

3. The benzidine hydrochloride method is much more rapid than the barium chloride method, for which reason it is very well adapted to routine water analysis. A determination can be had in 15 minutes.

4. The use of hydroxylamine hydrochloride eliminates the disturbing influence of iron.

5. Bicarbonate alkalinity has no effect upon the results.

--APPENDIX--

SOLUTIONS.

N/10 Sodium Sulphate was prepared by exactly neutralizing N/10 H_2SO_4 with N/NaOH. The SO_4 content was determined by precipitating and weighing as $BaSO_4$.

N/10 H_2SO_4 was prepared by diluting 52 cc. of C.P. concentrated H_2SO_4 (sp.g. 1.84) to 1 liter and diluting 100 cc. of this to 1 liter. Its exact strength was determined by titrating against pure Na_2CO_3, and also by precipitating the SO_4 as $BaSO_4$. From these values it was adjusted to exactly N/10.

N/10 HaOH was prepared by dissolving 4 grams of C.P. NaOH in 1 liter of carbon dioxide free water and keeping in a Jena bottle with a soda-lime tube in the stopper. The strength of the solution was determined by titration against the standard H_2SO_4.

The benzidine solutions were made up by weighing out the required amount of benzidine base; placing the same on an agate mortar, adding a small quantity of water, and working the whole up into a thin paste. This was then washed into a flask and made up to the required volume.

The hydroxylamine hydrochloride was a 10% solution in distilled water.

Data Used in Table 1.

Four series of waters were made up as follows:

a - 20 cc. of the N/10 Na_2SO_4 were diluted to two liters. 250 cc. of this solution contained .012 grams of SO_4 or 48 parts per million.

b - 40 cc. of the N/10 Na_2SO_4 were diluted to two liters. 250 cc. of this solution contained .024 grams of SO_4 or 96 parts per million.

c - 80 cc. of the N/10 Na_2SO_4 were diluted to two liters. 250 cc. of this solution contained .048 grams of SO_4 or 192 parts per million.

d - 160 cc. of the N/10 Na_2SO_4 were diluted to two liters. 250 cc. of this solution contained .096 grams of SO_4 or 348 parts per million.

e - 320 cc. of the N/10 Na_2SO_4 were diluted to two liters. 250 cc. of this solution contained .120 grams of SO_4 or 480 parts per million.

To 250 cc. portions of each of the above solutions were added the following amounts of benzidine in excess: 10, 15, 25, 35, 45, and 60 percents. Each determination was run in triplicate, by the method already described.

Data Used in Table I (cont'd.)

Data on solution A using 250 cc. for each determination with a final reaction volume of 500 cc.

Solution A = 48 p.p.m. SO_4

cc. of Benzidine 1cc. =.00065 SO_4	Excess Benzidine	cc. .05N NaOH	Grams SO_4	p.p.m. SO_4
20.4	10%	2.75	0.00650	26.0
20.4	10	2.70	0.00648	25.7
20.4	10	2.90	0.00696	27.8
21.3	15%	3.80	0.0095	38.0
21.3	15	3.85	0.0096	39.0
21.3	15	3.80	0.0095	38.0
23.1	25%	5.00	0.0120	48.0
23.1	25	5.00	0.0120	48.0
23.1	25	5.00	0.0120	48.0
24.9	35%	5.00	0.0120	48.0
24.9	35	5.00	0.0120	48.0
24.9	35	5.00	0.0120	48.0
26.7	45%	5.00	0.0120	48.0
26.7	45	5.00	0.0120	48.0
26.7	45	5.00	0.0120	48.0
28.8	60%	5.00	0.0120	48.0
28.8	60	5.00	0.0120	48.0
28.8	60	5.00	0.0120	48.0

Data Used in Table I (cont.)

Data on solution B using 250 cc. for each determination with a final reaction volume of 500 cc.

Solution B = 96 p.p.m. SO_4.

cc. of Benzidine 1 cc. = .00065 SO_4	Excess Benzidine	cc. .05N NaOH	Grams SO_4	p.p.m. SO_4
40.8	10%	8.33	0.00200	80.0
40.8	10	8.40	0.00202	80.8
40.8	10	8.53	0.00205	81.0
42.6	15%	9.10	0.00218	88.0
42.6	15	9.20	0.00220	88.0
42.6	15	9.18	0.00220	88.0
46.2	25%	10.00	0.00240	96.0
46.2	25	10.00	0.00240	96.0
46.2	25	10.00	0.00240	96.0
49.8	35%	10.00	0.00240	96.0
49.8	35	10.00	0.00240	96.0
49.8	35	10.00	0.00240	96.0
53.4	45%	10.00	0.00240	96.0
53.4	45	10.00	0.00240	96.0
53.4	45	10.00	0.00240	96.0
57.6	60	10.00	0.00240	96.0
57.6	60	10.00	0.00240	96.0
57.6	60	10.00	0.00240	96.0

Data Used in Table I (cont.)

Data on solution C using 250 cc. for each determination, with a reaction volume of 500 cc.

Solution C = 192 p.p.m. SO_4

cc. of Benzidine 1cc. = .00065 SO_4	Excess Benzidine	cc. .05N NaOH	Grams SO_4	p.p.m. SO_4
81.6	10%	19.0	0.00456	180
81.6	10	18.5	0.00442	179
81.6	10	18.0	0.00432	178
85.2	15%	19.30	0.00455	186
85.2	15	19.40	0.00463	187
85.2	15	19.25	0.00460	186
92.4	25%	20.00	0.00480	192
92.4	25	20.00	0.00482	192
92.4	25	20.00	0.00480	192
99.6	35%	20.00	0.00480	192
99.6	35	20.00	0.00480	192
99.6	35	20.00	0.00480	192
106.8	45%	20.00	0.00480	192
106.8	45	20.00	0.00480	192
106.8	45	20.00	0.00480	192
115.2	60%	20.00	0.00480	192
115.2	60	20.00	0.00480	192
115.2	60	20.00	0.00480	192

Data Used in Table I (cont.)

Data on solution C using 250 cc. for each determination, with a reaction volume of 500 cc.

Solution C = 192 p.p.m. SO_4

cc. of Benzidine 1cc. = .00065 SO_4	Excess Benzidine	cc..05N NaOH	Grams SO_4	p.p.m. SO_4
204.0	10%	41.65	0.100	400
204.0	10	41.60	0.999	399
204.0	10	41.80	0.105	401
213.0	15%	47.90	0.1150	460
213.0	15	47.90	0.1150	460
213.0	15	47.80	c0.1145	459
231.0	25%	50.00	0.1200	480
231.0	25	50.00	0.1200	480
231.0	25	50.00	0.1200	480
249.0	35%	50.00	0.1200	480
249.0	35	50.00	0.1200	480
249.0	35	50.00	0.1200	480
267.0	45%	50.00	0.1200	480
267.0	45	50.00	0.1200	480
267.0	45	50.00	0.1200	480
288.0	60%	50.00	0.1200	480
288.0	60	50.00	0.1200	480
288.0	60	50.00	0.1200	480

Data Used in Table 2.

The data in this table was obtained by using sodium sulphate solutions as before of varying concentrations with a stronger solution of benzidine (8 gms. per liter), the excess remaining constant.

A stock solution of 480 p.p.m. of Na_2SO_4 was made up by diluting 160 cc. of N/10 Na_2SO_4 to 1 liter. One liter of each of the following solutions was made up by diluting suitable quantities of the solutions containing 480 p.p.m. SO_4: 12, 24, 48, 96, 120, 240, 360, and 480 p.p.m. SO_4.

The benzidine solution was made up as previously described except that 8 grams per liter was used. Up to 48 p.p.m. the quantity of benzidine used was considerably more than 30%.

Data Used in Table 2.

250 cc. of each solution used.
300 cc. total volume.
30% excess benzidine.

p.p.m. SO_4	cc. .05N Na_2SO_4	Grams SO_4	p.p.m. SO_4 found	Error
10	1.25	0.0030	12.0	0.00%
10	1.26	0.00302	12.1	+0.80
10	1.25	0.00300	12.0	0.00
24	2.50	0.0060	24.0	0.00
24	2.50	0.0060	24.0	0.00
24	2.48	0.0054	23.6	-0.30
48	5.00	0.0120	48.0	0.00
48	5.00	0.0124	49.6	+1.20
48	5.00	0.0120	48.0	0.00
96	10.00	0.0240	96.0	0.00
96	10.00	0.0244	97.6	+1.60
96	10.00	0.0240	96.0	0.00
120	12.50	0.0300	120.0	0.00
120	12.50	0.0304	121.6	+1.30
120	12.80	0.0300	120.0	0.00
240	25.00	0.0600	240.0	0.00
240	25.50	0.0612	244.8	+2.00
240	25.00	0.0600	240.0	0.00
360	37.50	0.0900	360.0	0.00
360	38.00	0.0915	360.0	+1.10
360	37.50	0.0900	360.0	0.00
480	50.00	0.1200	480.0	0.00
480	51.00	0.1220	480.0	+1.70
480	50.00	0.1200	480.0	0.00

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